Available online at www.sciencedirect.com

SciVerse ScienceDirect

Physics Procedia 45 (2013) 97 – 100

Physics Procedia

ISS2012

Effect of oxygen-affinity additives on the superconducting properties of magnesium diboride

J.-J. Jang, J.-H. Ahn*

Department of Materials Engineering, Andong National University, 388 Songchun-dong, Andong, Gyungbuk 760-749, Korea

Abstract

We examined the effect of oxygen-affinity additives on the superconducting properties of magnesium diborides. The additives were elemental Y, Sm, Ca, Li compounds (LiH, $LiBH_4$), polyethylene and polyethylene glycol, which have a higher oxygen-affinity than magnesium. The formation of magnesium oxide during *in-situ* sintering of magnesium diboride was inhibited by the addition of such materials. The critical current density was not improved by the additives of Y, Sm, Ca and lithium compounds in spite of reduced oxide phases. Only the addition of polyethylene and polyethylene glycol resulted in the enhanced superconducting property.

Selection and/or peer-review under responsibilty of ISS Program Committee.

Keywords: Magnesium diboride; Superconducting materials; Ellingham digram; Polyethlylene; Polyethlylene glycol

1. Introduction

MgB_2 is an attractive superconducting material due to its high transition temperature, compositional tolerance, light-weight, non-toxicity and low material cost. However, the superconducting properties should be further improved for many practical applications. The synthesis of highly pure compound without oxides is one of challenging tasks for the improvement of superconducting properties of MgB_2 [1]. Magnesium has a high oxygen-affinity at high temperatures, forming oxides. During the in-situ synthesis of MgB_2 from the elemental powder mixture of Mg and B, thus, oxide phases such as MgO form almost inevitably due to a high susceptibility of magnesium at high temperatures.

To minimize this problem, we added oxygen-affinity elemental powders or compounds to MgB_2. The used additives in the present work were elemental Y, Sm ,Ca, and Li compounds (LiH, $LiBH_4$). According to the Ellingham diagram, the Gibbs free energy of oxidation of Y, Sm, Ca and Li is lower than that of Mg at temperatures above 700°C [2]. Some workers have examined the addition effect of rare earth oxides to MgB_2 [3], but we could not find no literature which deals with the addition of rare earth metals. What we expected from the addition of these materials was to reduce the formation of MgO during *in-situ* sintering at temperatures higher than 700℃, because the oxides of Y, Sm, Ca and Li might form more readily than those of Mg. We used elemental powders in the case of Y, Sm and Ca addition, whereas lithium hydrides (LiH, $LiBH_4$) were used for Li addition due to its high reactivity as an elemental form. We expected that the reducing element of hydrogen in the Li hydrides might further inhibit the formation of oxide. For comparison, we also used carbon- and hydrogen-containing polymers such as polyethylene ($C_{2n}H_{4n}$)) and polyethylene glycol($C_{2n}H_{4n+2}O_{n+1}$). The oxidation of carbon has a negative slope of line in the Ellingham diagram, showing a strong tendency of reduction of many oxides. Furthermore carbon has been known a very effective doping element for enhanced flux pinning of MgB_2 [4-6].

*Corresponding author. Tel.:+82-54-820-5648; fax: +82-54-820-6126.
E-mail address: jhahn@andong.ac.kr

Selection and/or peer-review under responsibilty of ISS Program Committee.
doi:10.1016/j.phpro.2013.04.061

2. Experimental details

The starting powders for the synthesis of MgB_2 were Mg(*Reidel-de-haen, <99.0%, 50 μm*) and B(*Merck, <99.0%, ~2 μm*). The additives were Y(*Acros Organics*, *99.9%, 40 mesh*), Sm(*Aldrich, 99.5%, 20μm*), Ca(*Aldrich*, 98%, 0.2~3mm), LiH(*Fluka*, 95%), $LiBH_4$(*Aldrich*), polyethylene(C_2H_4, *Aldrich*, 53~75μm), and polyethylene glycol(*Aldrich*).These elemental powders were mixed to give a nominal composition of MgB_2-X (X: 0.5, 1 and 5 at% additives. For *in-situ* sintering, the elemental powder mixtures were die-compacted at ambient temperature and sealed into evacuated quartz tubes, followed by sintering at 850°C for 24 h in an Ar atmosphere. The phase identification was carried out by a Rigaku D/Max 200 (XRD) and D/Max Rapid S (micro-beam XRD) diffactometer using Cu K_α radiation. The powder morphology and microstructure of the samples were examined by the scanning electron microscope (JSM-6300).The critical temperature (T_c) and the critical current density (J_c) were measured by a superconducting quantum interference device (SQUID) magnetometer at temperatures between 5 and 200 K. The T_c was determined as the onset of the diamagnetism.

3. Result and discussion

3.1. The addition of Y, Sm and Ca

Fig.1 shows the XRD patterns of MgB_2, doped with 0.5, 1 and 5 at% of Y, Sm and Ca. In the case of Y addition, an impurity phase of YB_4 phase formed additionally to MgB_2 even by 0.5 at% addition. The addition of Ca also resulted in the formation of undesirable CaB_6 and CaB_2O_4. In the case of Sm addition, on the other hand, no Sm-based impurity phase was visible by XRD. MgO phase was commonly detected in all samples. The amount of MgO was examined using a X'pert Highscore software. The result showed that the volume % of MgO reduced by the addition of Y, Sm and Ca to MgB_2. This is due to a higher oxygen affinity of these elements than Mg at the employed temperature of 850°C. According to the Ellingham diagram, it is expected that these elements are more readily oxidized than Mg, reducing the formation of MgO. The superconducting properties, however, did not improved by the addition of these elements.(Fig.2) The critical current density of Y- and Sm-doped MgB_2 was degraded due to the formation of harmful impurity phases such as YB_4, whereas that of Ca-doped MgB_2 remained unchanged by the addition.

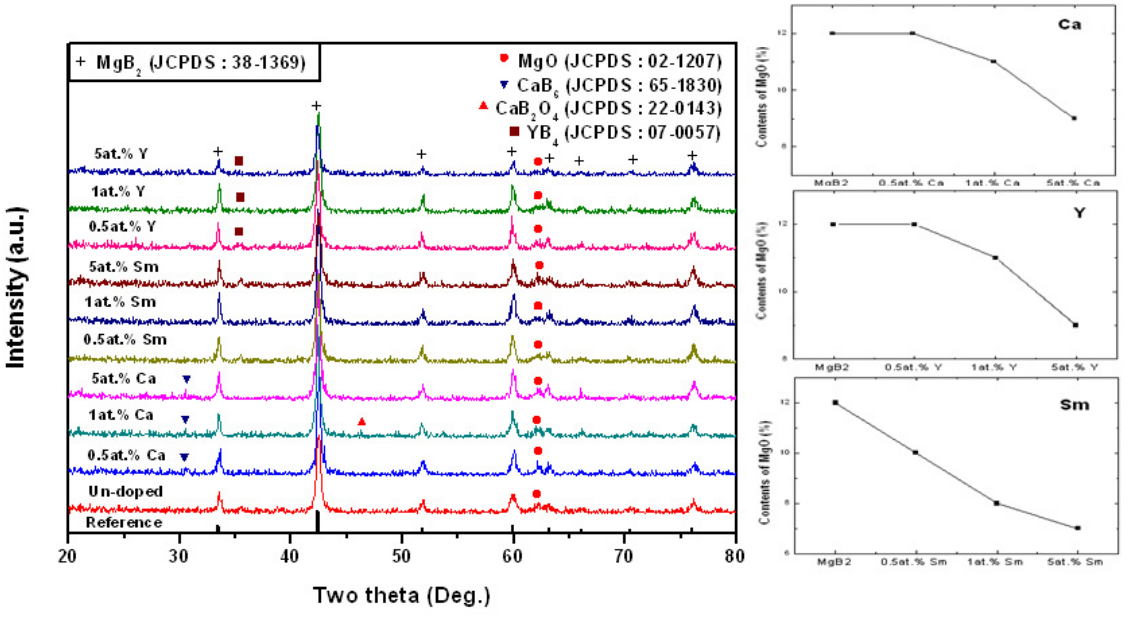

Fig 1. (a) XRD patterns and (b) the amount of MgO for Y-, Sm-, and Ca-doped MgB_2.

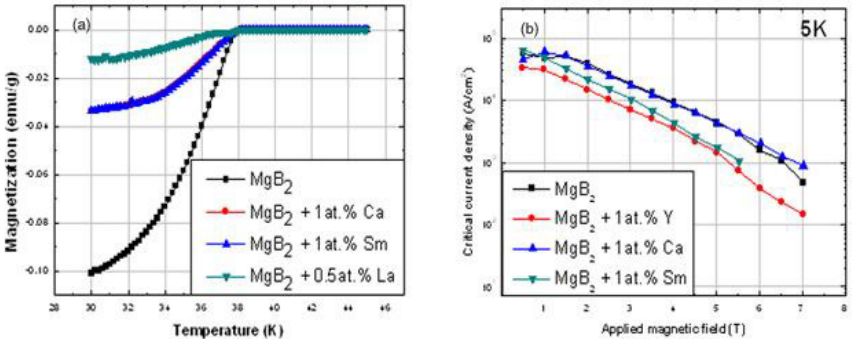

Fig 2. (a) Critical temperature (T_c) and (b) critical current density (J_c) of Y-, Sm-, and Ca-doped MgB_2.

3.2. The addition of LiH and $LiBH_4$

In the case of Li addition, we used lithium hydrides (LiH, $LiBH_4$) instead of metallic elements due to its high reactivity. As well, we thought that hydrides might be dissociated to radical hydrogen, facilitating the reduction of oxides [7]. However, the results of XRD showed that the addition of these compounds was not effective to reduce the oxidation of constituent metals (Fig.3). In the case of $LiBH_4$ addition, LiO_2 phase formed together with unreacted residual B. In the case of LiH addition, no impurity phase was visible by XRD. Contrary to expectation, the content of MgO increased by the addition of LiH_4. It is thought that the dissociated hydrogen reacts with residual oxygen to form magnesium hydroxides which in turn transform to MgO during sintering. As a result, critical current density was degraded, although T_c remained unchanged by the addition of Li hydrides (Fig.4).

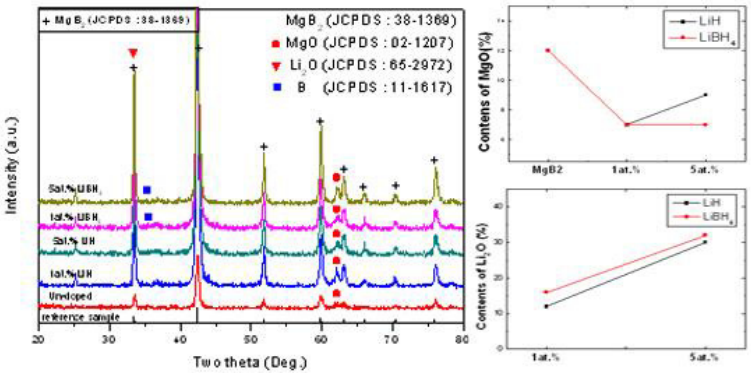

Fig 3. (a) XRD patterns and (b) the amount of MgO for Li compounds (LiH, $LiBH_4$) doped MgB_2.

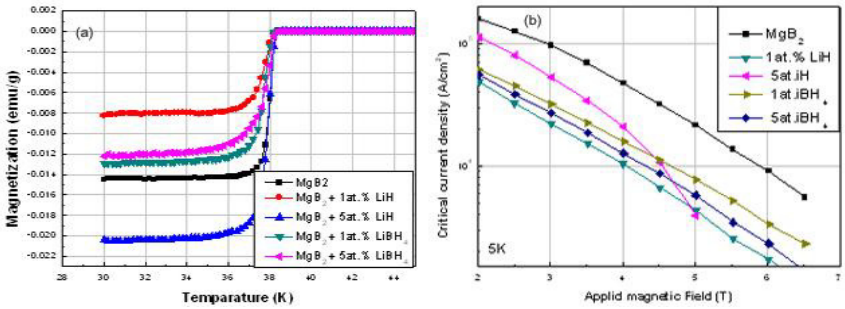

Fig 4. (a) Critical temperature (T_c) and (b) critical current density (J_c) of Li compounds (LiH, $LiBH_4$) doped MgB_2.

3.3. The addition of polyethylene (PE) and polyethylene glycol (PEG)

We examined whether the absence of oxygen-free polymers (PE; $C_{2n}H_{4n}$) inhibits the oxidation of oxide *via* reduction of metallic constituents by dissociated hydrogen. However, no big difference in the MgO formation was observed between the addition of PE and O-containing PEO. Compared to the above-mentioned Y-, Sm-, Ca- and Li-doped MgB_2, the addition of PE and PEO increased the amount of MgO rather than decrease. In spite of the increased MgO, the superconducting properties were markedly improved by the addition of these polymers due to well-known beneficial effect of carbon to MgB_2 [3-6].

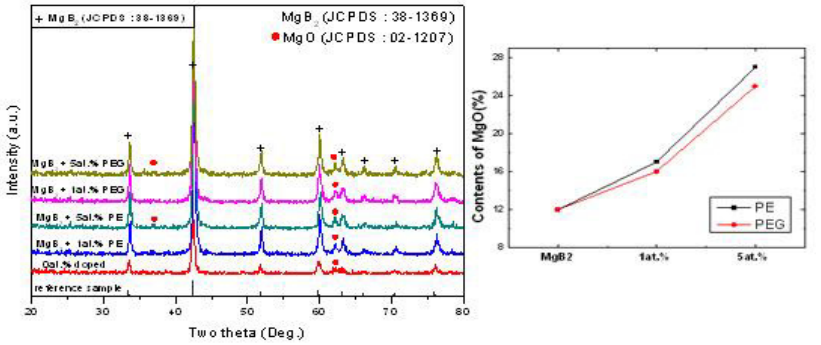

Fig 5. (a) XRD patterns and (b) the amount of MgO for polymers (PE, PEG) doped MgB_2.

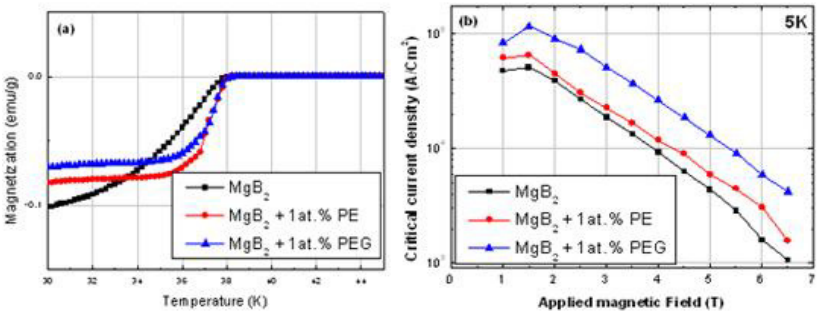

Fig 6. (a) Critical temperature (T_c) and (b) critical current density (J_c) of polymers (PE, PEG) doped MgB_2.

4. Conclusion

We have examined the oxygen-affinity additives to MgB_2 to reduce the formation of MgO. These elements were effective for the reduction of MgO, but the improvement of critical current density was not observed. Instead, the beneficial effect of carbon to MgB_2 was confirmed. Further study is needed to see the detailed effect of polyethylene.

Acknowledgements

This research was supported by the Basic Science Research Program (2010-0009978) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology.

References

[1] P. Kovac, I. Husek, T. Melisek, J. C. Grivel, W. Pachla, V. Strbik *et al.*, Supercond. Sci. Technol. 17 (2004) 41-46.
[2] E.H. Oelkers, H.C. Helgeson, E.L. Shock, D.A. Sverjensky, J. W. Johnson, V. A. Prokrovskii, J. Phys. Chem. 24 (1995) 1401-1600.
[3] Y. Katsura, J. Shimoyama, A. Yamamoto, S. Horii, K. Kishio, Physica C 463-465 (2007) 225-228.
[4] I. Maurin, S. Margodonna, K. Prassides, T. Takenobu, T. lto, D. H. Chi, Y. lwasa, A. Fitch, Physica B 318 (2002) 392-397.
[5] A. Bharathi, S.J. Balaselvi, S. Kalavathi, G.L.N. Reddy, S.S. Shastry, Y. Hariharan *et al.*, Physica C 370 (2002) 211-218.
[6] R.J. Cava, H.W. Zandbergen, K. Inumaru, Physica C 385 (2003) 8-15.
[7] P. Mauron, F. Buchter, O. Friedrichs, A. Remhof, M. Bielmann, C. N. Zwicky *et al.*, J. Phys. Chem. B 112 (2008) 906-910.